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EVALUATION OF EMULSION STEAM BLOCKING PROCESSES

Annual Report for FY 1985
Project OE3B

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EVALUATION OF EMULSION STEAM BLOCKING PROCESSES

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ABSTRACT

Laboratory work on this project started in late April 1984. During the first year of this project, FY 84, the effectiveness of emulsion blocking at elevated temperatures was demonstrated. Emulsions were identified that could be injected into cores, which reduced permeability up to 95 percent and withstood steam injection. It was found that dilute water-external emulsions were stable in fresh water (condensed steam) and had viscosities low enough for injection.

The work in FY 85 demonstrated blocking in cores with residual oil saturation, in situ generation of blocking emulsions, and the examination of surfactant blends that produce macroemulsions spontaneously or at least with minimum input of mechanical energy.

This report addresses Tasks 4-8 of project OE3B.

Task 4. In Situ Emulsification

In addition to the other laboratory experiments performed, core experiments showed that blocking emulsions can be produced by injection of emulsifiers. The permeability reductions ranged from 27 to 77 percent, and caustic was found to be a cost-effective emulsifier for most reservoirs which have been steamflooded.

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[1] Project Leader.

Task 5-6. Emulsion Injection

Core tests confirmed that injection of surface-produced emulsions could reduce permeability 30 to 91 percent, even when the pores were already partly "blocked" with residual oil. Tests were also performed by injecting emulsions into cores which had been steamflooded previously, then testing the stability of the emulsion block to continued steamflood. The emulsion block proved to be sufficiently stable at steam conditions to reduce the mobility of steam, but at steam temperature the effectiveness is sometimes reduced.

Task 7. Preparation and Testing of Emulsions Produced From New Oils Suggested by Client

In July-August of FY 85, it was decided to field test the procedure in Kern River Field, California. After obtaining oil, water, and core from that field, both emulsification tests and coreflooding tests were started.

Task 8. Alternative Surfactant Systems

Laboratory and core tests were conducted which compared six emulsification strategies. The results from the comparison are discussed within this report.

Conclusions

Emulsion blocks have proved to be stable to both hot water and saturated steam. The steamflood experiment with parallel cores demonstrated that emulsion injection can lead to an improved temperature profile during steamflooding and consequent incremental oil production.

Experiments performed with the Kern River core, oil, and water, although not yet completed, indicate the likelihood of a successful field test using surface-prepared emulsion in that field. *In situ* emulsification in that field may also be cost-effective, but this will be more difficult to predict with certainty.

INTRODUCTION

Background Information

The efficiency of many steamflood enhanced oil recovery (EOR) projects is severely affected by gravity segregation of low-density injected steam and higher-density reservoir (i.e. oil and water) fluids resulting in steam override near the top of the permeable reservoir layer where the oil saturation has been depleted. Cores taken from heavy oil reservoirs at the termination of a steamdrive clearly show this upward migration of the steam and consequent segregation of the displacing (steam) and displaced (oil and water) fluids. An effective method to increase the efficiency of a steamdrive is to plug or minimize flow in the high permeability, steam-swept override zone to direct steam to zones of higher oil saturation and thus improve the ratio of oil produced to steam injected.

Some producers of heavy oil utilizing steamflood techniques have adopted the method of foam injection or in situ foam creation as a mobility buffer to effect such a diversion of steam from the steam-swept zone. These foamblocks are created by injecting a relatively concentrated solution of foaming agent (surfactant and a noncondensible gas) with the flowing high-temperature, high-pressure steam. The noncondensible gas allegedly supports the foam structure, insofar as the steam would condense due to heat loss and collapse the foam if the inert gases were not present.

Current theoretical and laboratory analyses leave doubt about exactly how a foam increases the resistance to flow of steam within the steam-swept zone. If we consider that foam loses its macroscopic properties in pores smaller than 10 bubble diameters, then the theoretical possibility for foam flow exists only for rare cases (1).[2]

In early 1979, Broz hypothesized that the actual mechanism for steam diversion in these "foamblocks" is the accidental creation of plugging macroemulsions since thermally stable surfactant agents such as alkyl-aryl benzene sulfonates were being utilized as successful "foamers." Thus, it was

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[2] Underlined numbers in parentheses refer to the references listed at the end of this report.

conjectured that macroemulsion plugging may be an effective method for correcting steam override and may further be a dominant or adjunct mechanism in the heretofore perceived foamblocking technique.

A review of the literature produced several references relating to the use of emulsions as agents for causing permeability reduction. McAuliffe (2) demonstrated that injection of externally produced oil-in-water emulsions at 75° F effectively reduces the water permeabilities of sandstone cores. These laboratory findings were later substantiated by a successful field test of emulsion injection followed by waterflooding in the Midway-Sunset Field (3).

Several waterflood recovery process patents assigned to Texaco, Inc., describe laboratory core studies in which blocking emulsions were produced in situ by injection of surfactant mixtures (4-6). The conditions under which these experiments were performed (relatively high salinity, presence of divalent ions, crushed limestone cores) allow us to infer the creation of water-in-oil emulsions. Two later patents claim the procedure also applies to profile improvement for steamflooding (7,8). Cooke, in laboratory experiments, has observed that a viscous oil-external emulsion may be responsible for the large increase in pressure gradient that is observed immediately behind the displacement front during alkaline waterflooding under saline conditions (9). A recent waterflood patent (10) assigned to Mobil Oil Corp. relates to the creation of a plugging emulsion within a high salinity stratified reservoir. The surfactant/water/oil emulsion described in this patent is likely oil external.

Commencing in 1984, laboratory research at the National Institute for Petroleum and Energy Research has been conducted to test the ability of stable, plugging macroemulsions to displace and/or act as a mobility buffer for steam flowing in a porous medium and to investigate the commercial possibilities of such a technique.

Examination of available literature leads to the conclusion that NIPER is the first to demonstrate the effectiveness of emulsion blocking at elevated temperatures using water external emulsions. Results from the first year's research were presented at the UNITAR Conference on Heavy Oil Recovery (11).

Results of research on emulsion blocking in FY 84 (12) showed that it is effective and stable at elevated temperatures when emulsions are injected into oil-free cores using water external emulsions. The work in FY 85 demonstrated blocking in cores with residual oil saturation. The next phase, in situ generation of blocking emulsions, required examination of surfactant blends that produce macroemulsions spontaneously or at least with minimum expenditure of mechanical energy. The research goals for FY 85 were:

1. To test the method using a duplex core, with two intercommunicating selections in parallel, having different initial oil saturations, to simulate a steamed-out zone adjacent to an unflushed zone.

2. To purchase and construct facilities for performing steamflood tests both rapidly and economically, and to use that apparatus in emulsion blocking experiments.

3. To design a "micromodel" system (to be used in FY 86) which will allow the microscopic observation of the processes in the simulated reservoir pores, to identify the mechanisms, and distinguish between emulsion and foamblocking.

4. To continue the search for systems that produce macroemulsions (distinctly different from microemulsions) spontaneously.

The ultimate goal was the design of an optimum strategy for effective and permanent blocking that diverts steam to target areas of residual oil, possibly leading to a field test of the technique.

LABORATORY STUDIES (EXCEPT CORE FLOODING TESTS)

Spontaneous Emulsification Tests - Schechter & Wade Method (13)

Mobility control by blocking high-permeability zones with emulsions formed in situ requires agents that cause spontaneous emulsification to macroemulsions. Table 1 gives a representative selection of the many tests made to find such agents. The testing method was similar to that used by Cash and others. An examination of the results shows the following:

1. Surfactant-oil combinations that are reputed to emulsify spontaneously did form white material at the interface, but there was not much correlation with formation of large volumes of stable emulsions - even on shaking.

2. No consistent emulsification pattern was observed in comparing:
   a. Surfactant originally in water versus surfactant originally in oil.
   b. Formation of water-external or oil-external emulsions.
   c. Aqueous solutions with or without salt.

3. As reported previously, cyclic hydrocarbons showed the most tendency to emulsify. Sometimes linear hydrocarbons and crude oils formed a slight emulsion layer but only when the surfactant was first dissolved in the oil phase.

Spontaneous Emulsification Tests - Optimization by HLB

A systematic attempt to find an effective surfactant (one that will produce macroemulsions spontaneously) by optimizing the HLB (hydrophilic-lipophilic balance) was not successful. GAF-887, an ethoxylated alcohol with ehylene oxide number 29, has an HLB value of 17.2. Sandopan Liquid B, an ethoxylated sodium carboxylate with ethylene oxide number 1 has an HLB value of 6.0. These two surfactants were blended at a total concentration of 5 percent to yield an aqueous mixture of varying HLB. Without agitation, the surfactant mixture was then contacted with the crude oils. For Delaware-Childers and Wilmington oils, some "spontaneous emulsification" was observed at the interface only. Noone and Bartlett oils gave no effects.

Spontaneous Emulsification Tests - Dispersant Mixtures

Spontaneous macroemulsions can be formed readily in many cases by using a variation of the technique used in manufacturing agriculture sprays: dissolving the surfactant, with alcohol added, in the oil before contact with water (14). Since it is not possible to dissolve the surfactant into the crude oil in the reservoir, the dispersant mixture consists of surfactants dissolved in an oil-compatible solvent.

The dispersant that was formulated consists of sorbitan partial fatty acid ester, dodecylbenzene sulfonate, and isobutyl alcohol in methylisobutyl ketone. Upon contact with the Delaware-Childers crude oil and water, a macroemulsion forms spontaneously. A preliminary experiment was performed using this dispersant mixture. Sand (70 mesh) was packed into a 1.25 in wide by 5 in long glass tube. The sandpack was placed in a vertical position. Gravity flow (constant ΔP) was utilized to saturate the sandpack with oil and waterflood to residual oil.

After dispersant introduction, the flow rate was reduced to zero and would not resume until increased pressure caused the emulsion formed to be forced on through the sandpack. The sand was then cleaned and the dispersant again injected. In this case (no oil present in the sandpack), the flow rate did not significantly change, illustrating that oil must be present in the formation for the injectivity-reducing emulsification to be achieved. This experiment draws attention to the possibility that emulsion blocks will be more stable at constant pressure (more similar to field conditions) than at constant flow rate. The results are summarized in table 2.

Comparison of Surfactants - General Conclusions

Six oils, eleven surfactants designed for use in surfactant floods, and five surfactants designed for use as foamers were tested for comparison of surfactants designed for foaming with those designed for emulsification. Although exceptions occur, some general conclusions are as follows:

1. Emulsions produced by agitating aqueous surfactant mixtures and crude oils usually contain more oil than emulsions produced by contacting oil and foam.

2. When some foams are contacted with crude oil, very dilute oil-in-water emulsions form within the interfaces between the gas bubbles of the foam.

3. Driving foam through an oil-bearing zone results in more emulsion than simply contacting foam and oil.

4. More oil and emulsion are produced by waterflood after a foam slug has been driven through the oil zone than are produced during an equivalent waterflood without introduction of foam.

5. The only significant difference between surfactants classified as "foamers" and "non-foamers" is that foam is more stable for the surfactants which are classified as foamers.

Kern River Oil, Water & Core Studies

Three crude oils were added to the FY 85 emulsion blocking study. The oil of greatest interest was from the Kern River Field, California, and was furnished by Chemical Oil Recovery Co. Two samples were furnished, treated and untreated. Both samples are available in the field in sufficient quantities for preparing emulsions. Data in table 3 show that the produced oil contains a high percentage of bottom sediment and water. Consequently, the acid number is much lower than the treated (generator feed) oil.

In addition to the oil, two samples of water were received, softened and unsoftened. Both samples are low in total dissolved solids, but the unsoftened sample contains some divalent ions (see table 4).

Both oils would form emulsions with caustic (a cost-effective emulsifer) dissolved in both softened and unsoftened waters. However, caustic dissolved in softened water emulsified the oils much faster than caustic dissolved in unsoftened water. The treated oil, which is more uniform in texture, has the higher acid number and emulsifes more readily than the produced oil. The optimum conditions for forming the emulsion are given in table 5. A 2.5 percent emulsion prepared by dilution of a 75 percent oil-in-water emulsion is extremely stable after preparation.

Preparation of a concentrated (75 percent) emulsion with caustic followed by dilution with water is similar to the procedure which can be used in an oil field. The surface prepared emulsion would be diluted with water during injection.

Core material from the Kern River Formation was cleaned by Soxhlet extraction with toluene, in preparation for the coreflood sandpack tests.

The total acid number, TAN, (table 6) and mean droplet diameters (figure 1) were determined for emulsions produced from two other California crude oils which may be used in further work -- Freeman and Chaffee oils.

DEVELOPMENT OF APPARATUS

Steamflooding System

The tube furnace and control module necessary for completing the simplified steamflood system (figure 2) were received from Pacific Combustion. After completion, the system was tested using an 800-md Berea core that did not contain residual oil. This test proved the system capable of delivering steam to the core at appropriate temperatures and pressure. For example, at a flow rate of 2.1 cm^3/min (liquid water into furnace), steam entered the core at 398° F, and the pressure was 80 psig, approximately one-fourth the saturation pressure at that temperature. The arrival of a steam front at the core exit was indicated by the precipitous rise in temperature at that point, from 111° F to 212° F.

Duplex Core

To duplicate the effects of gravity override and channeling, a two-dimensional coreflood apparatus is needed. Coreflood experiments were performed using the duplex core illustrated in figure 3. The core is constructed by sandwiching together two slices of Berea sandstone. The upper half of the core is a high-permeability zone which contains no oil. The lower half of the core has a lower effective permeability due to the residual oil in that zone. For the experiment to simulate what can happen in a petroleum reservoir previously steamflooded, the spacer separating the upper and lower halves must be permeable.

Parallel Core

The arrangement of two separate core holders (figure 4) has the disadvantage of not allowing communication between the two separate zones. The advantage of this arrangement, however, is that when steam invades the high permeability core, the low-permeability zone is not simultaneously heated and remains at native reservoir temperature. This is probably more like the temperature profile to be expected in a reservoir being steamflooded -- a hot steam-swept zone above a cooler unswept zone.

Micromodel

The visual observation of fluid flow at the pore level should be of considerable utility for evaluating the behavior of dilute emulsions in porous media. Micromodels can be constructed by sandwiching a thin section of sandstone between two glass plates, etching a pore pattern into one or both glass plates, or by annealing glass shot between glass plates. A low power (long working distance) microscope is then used for pore level observation during fluid injection.

In FY 85, a design was selected for the micromodel system, and materials have been ordered. The model will be used for mechanistic studies in FY 86 to determine the role played by emulsions in so-called "foam blocks."

Sandpacks

Since consolidated Berea cores are not representative of most reservoirs amenable to steamflooding, sandpacks were prepared by packing sand into Teflon sleeves and placing the sleeves in Hassler core holders. By using the Hassler holders and teflon sleeves, a constant overburden pressure can be applied to the sandpack. This is an advantage over conventional sandpacks. Sandpacks were prepared from the Kern River core received from Chemical Oil Recovery Co.

CORE FLOOD TESTS

Emulsion Injection - No Residual Oil

Table 7 presents results of a test with saturated steam at 320° F and 75 psig. The first part of the test showed that steam itself would not alter the permeability. The second part showed that an emulsion block, once formed, was not degraded by the injection of steam. The emulsion was 0.5 volume-percent Wilmington oil, formed with 0.42 percent caustic.

Table 8 presents results of a test with saturated steam at 300° F and 52 psig. The sandpack was prepared as described above from the cleaned Kern River core material. The initial permeability of the sandpack was 1624 md.

A 75 percent oil-in-water emulsion was prepared by allowing treated (generator feed) oil to react with 0.5 percent sodium hydroxide. This emulsion was then diluted to 2.5 percent before injection. One half pore volume of the emulsion was injected, and the permeability dropped to 397 md, a reduction of 76 percent. One-half pore volume of a steam-swept zone is economically viable should a field test be performed. An additional 0.5 pore volume of the emulsion was injected, lowering the permeability to 226 md.

The steam stability of the emulsion block was tested by injecting steam at 300° F. After steam injection, the permeability was to 406 md, still a 75 percent reduction in effective permeability.

Emulsion Injection - With Residual Oil

Tests 11, 12, and 13E (table 9) confirmed that injection of an externally produced emulsion could reduce permeability 30 to 56 percent, even when the pores were already partly "blocked" with residual oil. Test 11 was performed by injecting the emulsion immediately after waterflood to residual oil. Tests 12 and 13E were performed by injecting emulsion after tertiary recovery by surfactant flooding. The surfactant flood was 0.1 PV Floodaid 141, optimized for the crude oil, and 0.4 PV of 27 cp Pusher 500 solution.

Emulsion Injection - Residual Oil After Steam

In tests STF-3 and STF-4 (table 10), the emulsions were injected after high-permeability cores were saturated with Wilmington oil and then steamflooded. In test STF-3, emulsion injection lowered the permeability by 91 percent; however, subsequent injection of 380° F, 40 psig steam resulted in destruction of most of that emulsion block.

In test STF-4, emulsion injection lowered the permeability by 85 percent, and that emulsion block was stable to the subsequent injection of 350° F steam.

Emulsion Injection - Parallel Cores

The duplex core arrangement presents one serious drawback in trying to stimulate gravity override. Even though the steam at first invades only the high-permeability, oil-free zone, the lower oil-containing zone is also heated because of heat transfer through the steel core holder. The resultant heating of the lower zone decreases oil viscosity, resulting in oil production and increased mobility of steam through that zone. To avoid this problem, the arrangement consisting of two separate core holders shown in figure 4 was made.

The results of the parallel core experiment are given in table 11. A Berea core containing residual Wilmington oil (18.4° API) was connected in parallel with a core which did not contain oil. Saturated steam at 310° F injected for 3 hours at constant mass flow rate produced 11 percent of the oil-in-place from the oil-containing core. After an externally produced emulsion was injected, saturated steam was injected for 3 hours at the same steam temperature which resulted in production of 34 percent of the oil-in-place. At the conclusion of this experiment, the effective permeability of the high-permeability zone (oil-free) was reduced by 85 percent. To maintain saturated steam conditions at the appropriate temperature, the mass flow of water to the steam generator also had to be reduced after emulsion injection. The outlet temperature from the oil-containing core increased after emulsion injection, indicating higher flow rate through that core.

In Situ Emulsification - Caustic Injection

Table 12 lists results of experiments 14, 15, 17, and 18 were performed by injecting sodium hydroxide slugs into cores containing residual Wilmington oil. The most promising was the injection of nonsaline caustic into a core with oil saturation below normal waterflood residual, resulting in a 43-percent decrease in the effective permeability.

The test with saline caustic presumably produced an oil-external emulsion that was displaced in the tertiary mode and raised the effective permeability to water. This observation led to core tests 16 and 19, which are discussed in the section on in situ emulsification with surfactants.

To duplicate the effects of gravity override and channeling -- a two-dimensional model -- two duplex core experiments were performed. This type of core is described above and is illustrated in figure 3. The upper half of the core is a high permeability zone which contains no oil. The lower half of the core has a lower effective permeability due to the residual oil present. For the experiment to represent what might actually happen in a petroleum reservoir previously steamflooded, the spacer separating the halves must be permeable. The first of these experiments was abandoned because the spacer appeared to be compressed into a impermeable layer.

In the second experiment, 24A, a rubber spacer with 3/32 in. holes was used. The injection of 0.47 PV emulsifier (1.06 percent NaOH) reduced the permeability to water from 367 to 166 md. This reduction (54.8 percent) presumably resulted from emulsion produced in the low-permeability zone. The emulsion has migrated into the higher permeability zone. No emulsion or oil was produced at the core exit, and examination of the core sections did not reveal a positive explanation. The results of the experiment do support the possibility of using an emulsion block produced _in situ_ to control gravity override and are given in table 13.

In situ emulsification coreflood experiments with Kern River oil, sandpacks constructed from Kern River core material, and caustic were in progress at the end of FY 85, but not completed.

In Situ Emulsification - Surfactant Injection

The results of test 15 which produced an oil-external emulsion (saline caustic) suggested a pair of core tests with surfactant injections. The systems in corefloods 16 and 19 produced spontaneous emulsions (table 14). The coreflood with the toluene-saturated core (test 16) produced an oil-external emulsion when surfactant was injected into the core, and the effective permeability to water increased; the coreflood with the benzene-saturated core (test 19) produced a water-external emulsion, and there was substantial blocking.

This confirms previous results that indicate water-external emulsions cause permanent (for many pore volumes) permeability reductions, while the formation of oil-external emulsions causes temporary permeability reductions.

In tests 9, 10, and 13 (table 15), the emulsifying surfactant was 3.75 weight percent Petrostep 420 + 2.5 percent Alipal SE-463. Tests 9 and 10 were performed by injecting the emulsifying surfactant mixture immediately after waterflood. In test 10, the salinity was 8.5 percent (and contained divalent ions). High salinity favors formation of water-in-oil emulsion, and after temporary decrease in the effective permeability, the effective permeability increases due to the mobilization of significant oil.

Test 9, which we assumed would form oil-in-water emulsion, also produced some oil and showed an increase in the effective permeability to water. This suggested repeating the experiment but producing some of the oil by an EOR method in the tertiary mode. Thus the residual oil saturation was reduced before injecting the surfactant mixture designed to cause formation of macroemulsion blockage. When this experiment was done (test 13), the results showed that blocking by in situ emulsification is effective when residual oil is not mobilized. These results agree with those reported previously in table 12 for tests 14, 15, 17, and 18 which were in situ emulsification tests performed with caustic.

In Situ Emulsification - Dispersant Injection

Two experiments were performed using Delaware-Childers oil and a dispersant mixture (DDBS, ATPET 200, IBA, MIBK). In both experiments the core was saturated with oil and then waterflooded to residual oil. See table 16.

The first experiment, 20, was performed at constant flow rate (0.86 ml/min) and even though 15.6 ml of oil was produced after dispersant introduction, the effective permeability increased only slightly.

The second experiment, 26, was performed at a similar initial flow rate, but at constant pressure. Injection of 0.02 PV emulsifier at constant pressure (similar to field conditions) resulted in a long-term reduction of 77 percent in permeability.

Both experiments were designed to form oil-in-water emulsions in situ. The significant result is that blocking by the emulsion appears to be most stable at constant pressure flood which is similar to oil field conditions.

SUMMARY AND CONCLUSIONS

The six injection strategies considered in this research are listed in table 17. Emulsions have been produced external to the core with aqueous surfactant mixtures and with aqueous caustic. Injection of those emulsions resulted in permeability decreases of 33 to 95 percent in oil-free cores and cores containing residual oil. Dispersant mixtures can also be used for producing emulsions external to the core, but this was not done.

For *in situ* emulsification (to macroemulsion) aqueous caustic shows much promise -- resulting in permeability reductions from 27 to 55 percent. Energy is required for emulsification to macroemulsion, and this energy is furnished, in part, by diffusion of the caustic-generated surfactants across the interface from oil to water. Tests with dispersant mixtures indicate this procedure may also be of use for *in situ* emulsification and the resultant well fluid intake profile improvement. Aqueous surfactant mixtures generally have not effectively produced macroemulsions *in situ*, although some tests have caused reductions in permeability despite the mobilization of oil that often occurs. Some factors which work against *in situ* emulsification with aqueous surfactants are (1) low oil saturation within the steamflooded zone, (2) oil remaining in the steamflooded zone is altered in composition, and (3) inadequate mixing energy.

Emulsion blocks have proved to be stable to both hot water and saturated steam, with one exception. Oil-in-water emulsions are more effective than water-in-oil emulsions for reducing fluid flow in high permeability cores. These emulsion "blocks" are stable to many injected pore volumes of hot water. The stability to saturated steam is also reasonably good, but superheated steam rapidly degrades the effectiveness of emulsion blocks. The steamflood experiment with parallel Berea cores demonstrated that emulsion injection can lead to an improved temperature profile during steamflooding and consequent incremental oil production.

Experiments performed with the Kern River sandpacks, oil, and water, although not completed, indicate the likelihood of a successful field test using surface prepared emulsion in that field. *In situ* emulsification in that field may also be cost effective, but this will be more difficult to predict.

In FY 86, the most interesting results should be obtained from the anticipated field tests which are now being designed to test the emulsion blocking techniques developed in the past year. A micromodel is being constructed which will be used for mechanistic studies of emulsion and foam blocking. This will allow understanding of the role played by macroemulsions in "foam drive" and accordingly provide information useful in designing more efficient systems to recover incremental oil. Two other areas to be investigated are the degree to which emulsions can penetrate the steam swept zone and the degree of losses expected when transporting the emulsifier (caustic or surfactant mixtures) into the zone.

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TABLE 1. Spontaneous emulsification tests with 3% TRS 10-80.

	1% NaCl						No Salt					
	Surf. dissolved in aq.			Surf. dissolved in oil			Surf. dissolved in aq.			Surf. dissolved in oil		
Oil	I	B	T	I	B	T	I	B	T	I	B	T
benzene	Y[d]	0	0/W[a]	N[e]	Sl[c]	-	Y	Y	0/W	N	N	-
toluene	Y	Y	W/0[b]	N	sl	-	Y	Y	W/0	Y	Y	W/0
methyl cyclohexane	sl	sl	-	N	N	-	N	sl	-	N	N	-
n-decane	N	N	-	sl	sl	-	N	N	-	Y	Y	W/0
n-octane	N	N	-	sl	sl	-	N	N	-	Y	Y	W/0
Delaware-childers	N	N	-	N	sl	-	N	N	-	Y	N	-
Noone	N	N	-	N	N	-	N	N	-	N	N	-
Bartlett	N	N	-	N	N	-	N	N	-	N	N	-

I = Interface, B = Bulk, T = Type of emulsion, Surf = Surfactant, aq = aqueous

a - o/w = water external emulsion

b - w/o = oil external emulsion

c - sl = slight amount of emulsification

d - Y = large volume of emulsion formed

e - N = no emulsion formed

TABLE 2. Gravity flow sandpack experiment.

1¼" X 5" Sandpack
70 mesh sand
Delaware Childers Oil

32.5% Sorbitan partial fatty ester	dispersant mixture
35.0% Dodecyl Benzone Sulfonate	
28.7% Methylisobutyl ketone	
3.8% Isobutyl alcohol	

Procedure	Gravity Flow (ml/min)
Inital water	7.1
Waterflood (residual oil)	1.7
Dispersant introduction	0
Pressure-out dispersant and free oil, waterflood	0.3
Pressure-out emulsion, waterflood	5.0
Clean sand, waterflood	8.3
Dispersant introduction	6.2
Waterflood	6.2

TABLE 3. Kern River Oil.

	Oil	
	Produced	Treated
Specific Gravity @ 60°/60° F, degrees	0.9892	0.9868
A.P.I. Gravity, degrees	11.5	11.9
Saybolt Viscosity @ 130° F, s.y.s.	-	6379.4
Kinematic Viscosity @ 130° F, centistoke	-	1374.5
Density, gm/cm^3 @ 60° F	0.9882	0.9858
Bottom Sediment and Water, vol. %	50.0	2.0
Total Acid Number, mg/gm	1.331	2.364

TABLE 4. Kern River Brine.

	Brine	
	Produced	Softened
Total Dissolved Solids, mg/l	718	722
Magnesium, mg/l	1.1	0
Calcium, mg/l	10.5	0

TABLE 5. Optimum conditions for Kern River emulsion preparation.

Oil	Treated (Generator Feed)
Water	Softened
Emulsifier	0.5 percent NaOH
Step 1 Emulsion	75. percent oil-in-water
Step 2 Emulsion	2.5 percent oil-in-water

TABLE 6. Emulsions Made With Freeman and Chaffee oils.

Oil	Total Acid No.	Emulsifier	Emulsion Type	Mean Droplet Diameter, microns
Freeman	2.8	0.25% NaOH	O/W	33.2
Freeman	2.8	SE-463[a]/P420[b]/MIBK[c]	O/W	33.3
Chaffee	1.4	SE-463/P420/MIBK	O/W	26.0

a. Sodium salt of alkylaryl polyether sulfonate

b. Petrostep medium equivalent weight petroleum sulfonate

c. 4-methyl - 2-pentanone

TABLE 7. Steam stability of emulsion block.

Core: Berea, 24" x 1½" diam.
Emulsion: 0.5 vol. % Wilmington oil

	Temperature, °C	Permeability, md
Initial, water	22	81.7
Steam	153	-
Water	24	89.3
After 6.5 PV emulsion	22	21.0
Steam	161	-
Water	23	21.6

TABLE 8. Injection of 2.5% emulsion into Kern River sand.

Absolute permeability, md	1624
Permeability after 0.5 PV emulsion, md	397
Permeability after 1.0 PV emulsion, md	226
Permeability after 300° F steam, md	406

TABLE 9. Tests of emulsion injection with residual oil present.

Test #	Oil	Effective permeability, md after waterflood	Effective permeability, md after surfactant	Emulsion Injected, PV	Effective permeability, md after emulsion	Oil produced, % PV
11	*DC	33	-	10	16	6
12	DC	-	27	7	18	-
13E	DC	-	84	8	32	-

* Delaware-Childers Oil

TABLE 10. Injection of externally produced emulsions into cores containing residual oil. Wilmington Oil - after steam.

Test #	Emulsion Injected, PV	Permeability Absolute, md	Permeability Before Emulsion, md	Permeability Final, md	Permeability Reduction, %	Flow Rate, cm^3/min
STF-3	8.1	1436	862	79	91	3.4
STF-4	8.2	823	744	108	85	3.4

TABLE 11. Parallel core experiment. Wilmington Oil - saturated steam.

	Cores		
	W/Oil	Oil Free	Overall
Absolute permeability, md	150	222	-
Effective permeability after waterflood, md	14	222	105
Volume steam injected, (as water), cm^3	-	-	330
Steam temperature, ° F	310	310	310
Outlet temperature, ° F	104	214	-
Oil produced, %	11	-	-
Effective permeability, md	-	-	98
Volume emulsion injected, cm^3	-	-	550
Effective permeability, md	-	-	13
Volume steam injected (as water), cm^3	-	-	108
Steam temperature, ° F	314	314	314
Outlet temperature, ° F	148	213	-
Oil produced, %	34	-	-
Effective permeability, md	11	33	20

TABLE 12. *In situ* emulsification formation. Wilmington Oil - 50° C.

				Permeability				
Test #	Emulsifier	Emulsifier Injected, PV	Water	Absolute, md	Before Emulsion, md	Final, md	Reduction, %	Flow Rate, cm^3/min
14	0.55% NaOH	0.45	Fresh	325	45	33	27	3.4
15	1.06% NaOH	.46	1.06% Nacl	290	22	51	--	3.4
17	1.06% NaOH	0.47	Fresh	257	24	18	25	3.4
18	1.06% NaOH	0.83	Fresh	1,400	88	50	43	3.4

TABLE 13. Duplex core tests - *in situ* emulsification.
Wilmington Oil - 50° C

Run	Injection	Permeability Absolute (md)	Initial (md)	Final (md)	Reduction (%)
24	1.06% NaOH	800	--	--	N/A
24A	1.06% NaOH	800	367.0	166.0	54.8

TABLE 14. *In situ* emulsification experiments with w/o and o/w systems.

Test Number	Absolute Permeability (md)	Oil	Injected Emulsifier (PV)	Effective Permeability (md) Before Emulsifier	After Emulsifier	Emulsion Type
16	312	toluene	0.40	15	60	w/o
19	522	benzene	0.20	27	17	o/w

Emulsifier: 3% Witco TRS 10-80 Petronate

TABLE 15. Tests of *in situ* emulsification.

		Effective permeability, md		Emulsifier Injected		Effective permeability, md	
Test #	Oil	after water-flood	after surfactant	PV	Water	after emulsifier	Oil produced
9	*DC	20	--	0.2	Fresh	60	some
10	DC	19	--	0.8	8.5% Brine	65	14
13	DC	--	108	0.1	Fresh	84	-

Emulsifier: 3.75% Petrostep 420 + 2.5% Alipal SE 463

TABLE 16. _In situ_ emulsification by dispersant mixture.

Test Number	Absolute Permeability (md)	Oil	Flow Condition	Injected Dispersant (PV)	Effective Permeability (md) Before Dispersant	Effective Permeability (md) After Dispersant
20	225	*DC	Constant Flow (.86 ml/min)	0.02	63	68
26	330	DC	Constant Pressure (initially 0.08 ml/min)	0.02	31	6.9

* Delaware Childers Oil

TABLE 17. Comparison of injection strategies.

Aqueous Surfactant	external	33-95% reductions in permeability. Works best with lighter oils.
	in situ	Results in increased relative permeabilities due to oil production and microemulsions.
Aqueous Caustic	external	76-88% reductions in permeability. Best with heavy, acidic oils.
	in situ	27-55% reductions in permeability. Best with heavy, acidic oils.
Dispersant Mixture	external	Not tried, but would expect results similar to other external emulsion injections.
	in situ	0-77% reductions in permeability. Best at low flow rates (1 ft/day) at constant pressure. Good with light and heavy crudes.

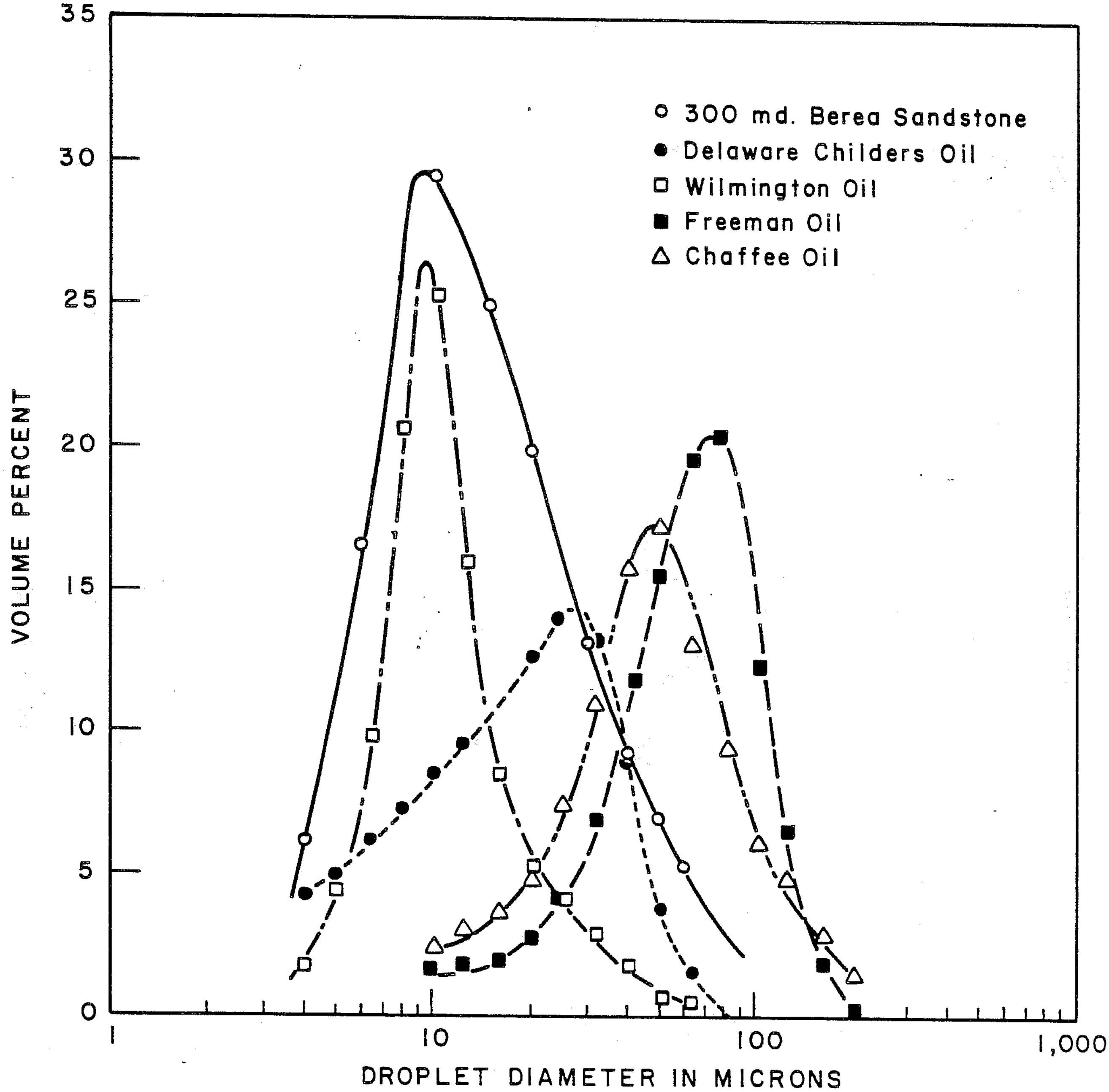

FIGURE 1. Droplet size distribution for o/w emulsions.

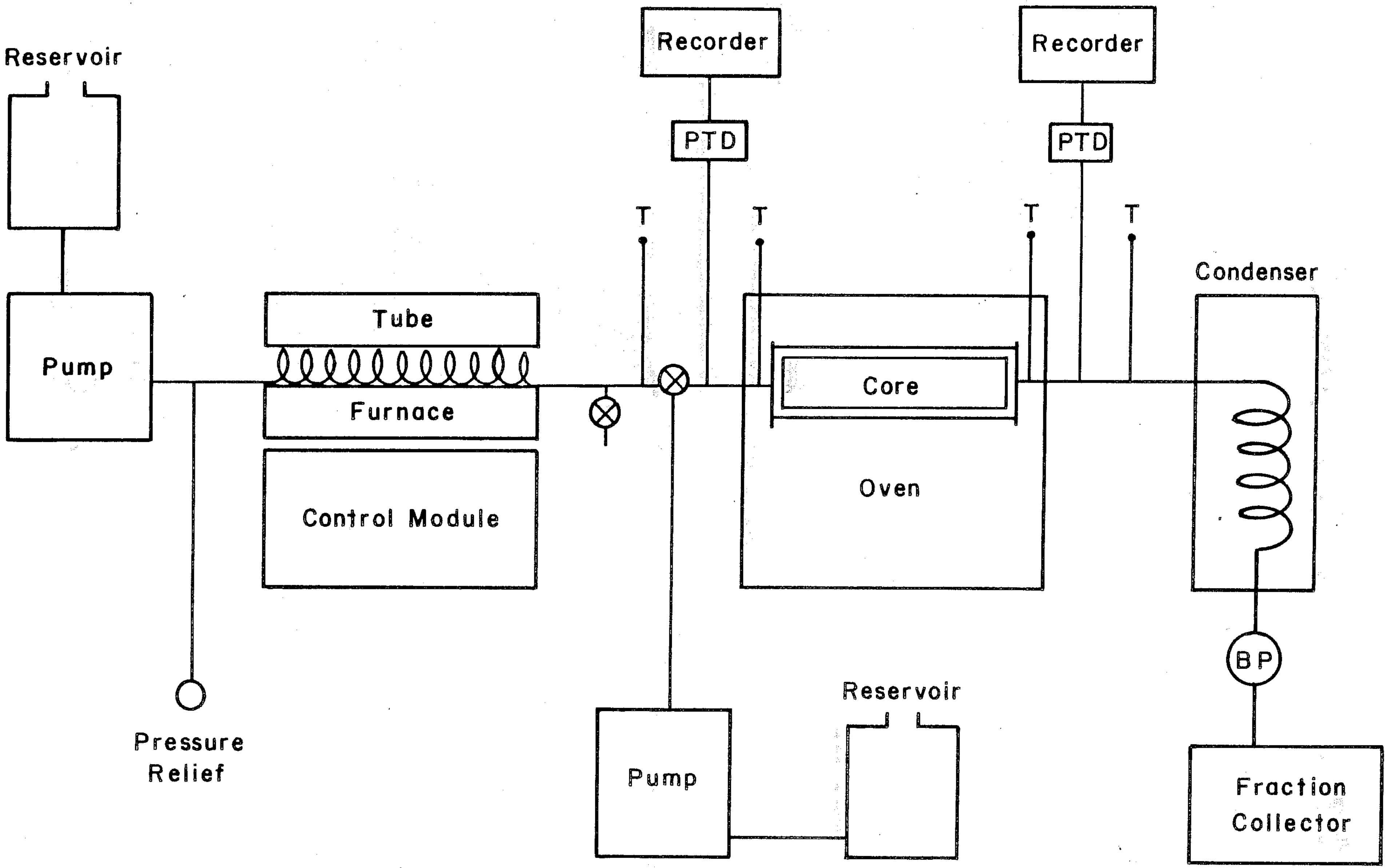

FIGURE 2. Simplified steamflood system.

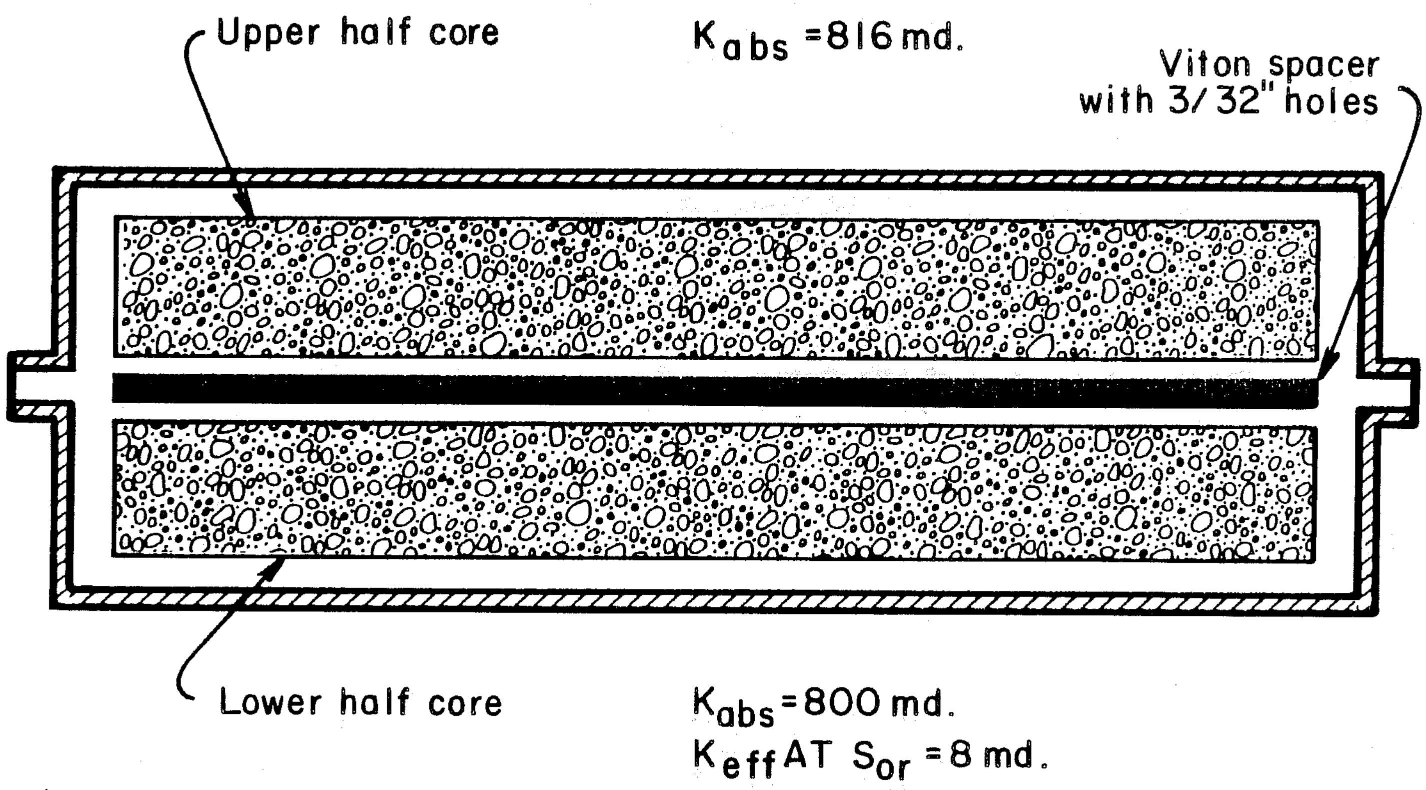

FIGURE 3. Duplex core arrangement.

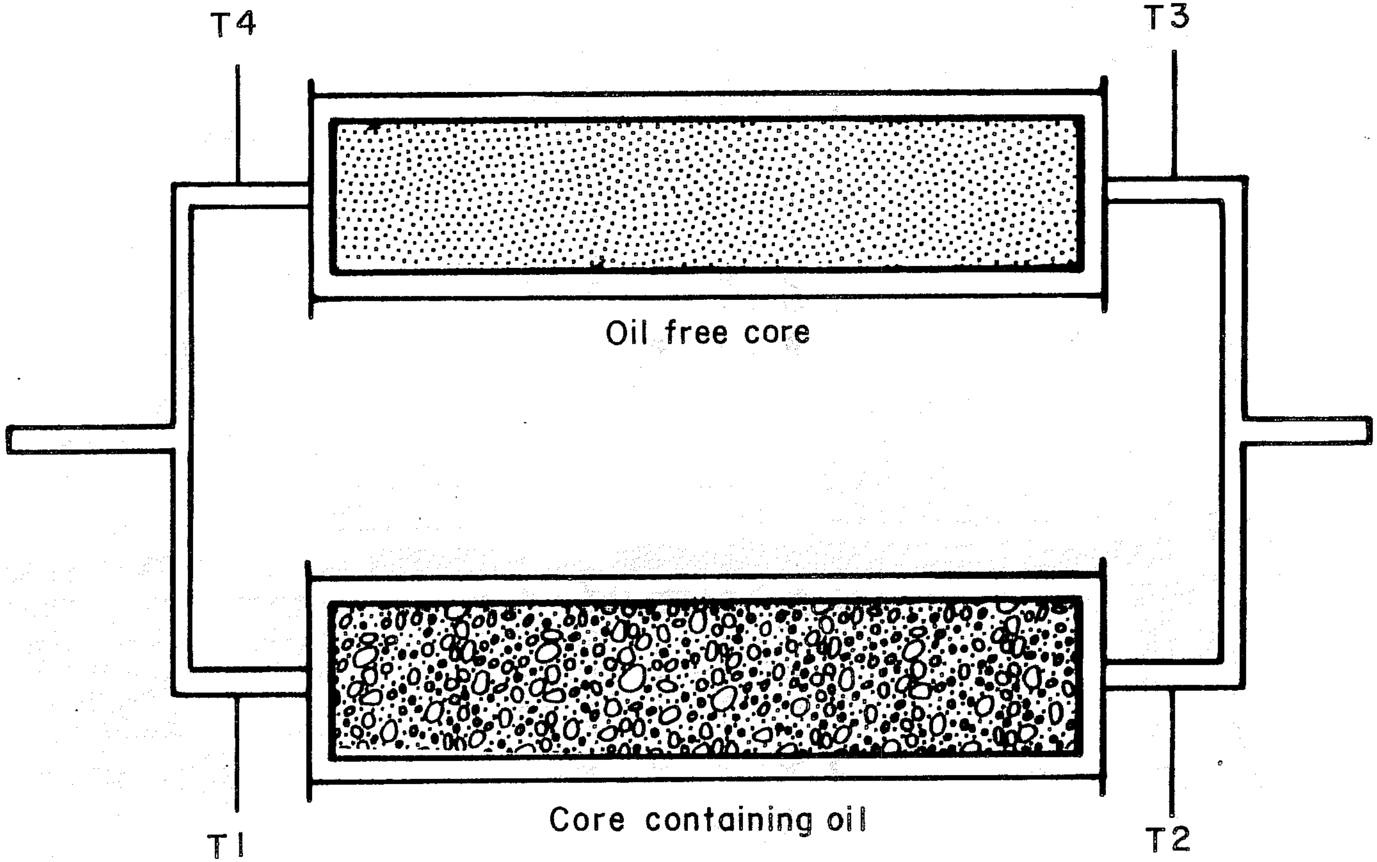

FIGURE 4. Parallel cores.

APPENDIX A

BLOCKING OF HIGH PERMEABILITY ZONES IN STEAMFLOODING BY EMULSIONS

by

J. S. Broz, T. R. French, and H. B. Carroll

Unitar Conference on Heavy Oil Recovery
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BLOCKING OF HIGH PERMEABILITY ZONES IN STEAMFLOODING BY EMULSIONS

by
J. S. Broz[1], T. R. French[2], and H. B. Carroll[2]

Abstract

It is well-known that the economics of many steamflood EOR technologies are strongly affected by steam override (gravity segregation) and steam channeling. The economic performance of many steamfloods can be improved if an effective method of plugging the steam override or channeling zones is utilized. Traditionally, "foam" blocking techniques have been utilized with variable success to achieve these goals.

In this paper, the first-phase of laboratory results in the development of a new emulsion blocking technique for the correction and control of steam override and channeling are presented. Coreflood experiments were performed to demonstrate the effectiveness of emulsion blocking at temperatures ranging from ambient to 160° C. The permeability reduction of various types of cores using externally produced emulsions and *in situ* generated emulsions was measured for light and heavy crude oils. Externally produced emulsions injected into oil-free cores reduced the permeability by 86 percent at 110° and 77 percent at 160° C. Emulsions generated *in situ* using a caustic emulsifier with Wilmington crude oil achieved a 43 percent reduction in effective permeability with the absolute permeability of this core being 1,400 md. In both cases of injected and *in situ* emulsions the emulsion block was thermally stable and no time-degradation of the block was observed.

The strong possibility that "foamblocks" as heretofore applied may have an emulsion blocking component to the overall plugging mechanism is discussed. Foams created with known foaming agents were contacted with various crude oils and the authors observed emulsified droplets within the liquid interfaces.

INTRODUCTION

The efficiency of many steamflood enhanced oil recovery (EOR) technologies is severely affected by the gravity segregation of the low-density injected steam and the high-density displaced reservoir fluids resulting in steam override near the top of the permeable reservoir layer where the oil saturation has been depleted. Cores taken from heavy oil reservoirs at the termination of a steam drive clearly show this upward migration of the steam and consequent segregation of the displacing (steam) and displaced (oil and water) fluids. An effective method to increase the efficiency of a steam drive is to plug the high permeability steam-swept override zone in order to direct steam to zones of higher oil saturation and thus improve the ratio of oil produced to steam injected.

Some heavy oil producers utilizing steamflood techniques have adopted the method of foam injection or *in situ* foam creation as a mobility buffer to effect such a diversion of steam from the steam-swept zone. These so-called "foamblocks" are created by injecting a relatively concentrated solution of foaming agent (surfactant and perhaps a noncondensible gas) with the flowing high-temperature, high-pressure steam. The noncondensible gas allegedly supports the supposed foam structure, insofar as the steam would condense due to heat loss and the foam would collapse if the inert gases were not present.

To date there is no conclusive theoretical or laboratory analysis of exactly how a foam would increase the resistance to flow of steam in the steam-swept zone, and further there is no direct or indirect evidence of actual foam formation in the porous structure of the reservoir medium. Work performed at New Mexico State University (Holbrook, et al., 1981), however showed that foam viscosities are generally an inverse function of foam density. Thus, in areas where gas (steam) fingering is pronounced, these researchers postulated that foam viscosity would increase with gas saturation and thereby tend to mitigate steam channeling. Although foam is pseudoplastic (non-Newtonian) in character, the theoretical rheology of foam flow in a porous medium is not consistent with the mobility buffering concept for steam because of low yield points and high inherent compressibilities of the foam structure.

In early 1979, it was hypothesized by one of the authors that in effect what may be the actual mechanism for steam diversion in these "foamblocks" is the accidental creation of plugging macroemulsions since thermally stable surfactant agents such as alkyl-aryl benzene sulfonates were being utilized as successful "foamers". Thus, it was conjectured that macroemulsion plugging may be an effective method for correcting steam override and may further be a dominant or adjunct mechanism in the heretofore perceived foamblocking techniques.

LITERATURE BACKGROUND

A review of the literature resulted in several references relating to the use of emulsions as agents for causing permeability reduction. McAuliffe demonstrated that injection of externally produced oil-in-water emulsions at 75° F effectively reduces the water permeabilities of sandstone cores (1973). These laboratory findings were later substantiated by a successful field test of emulsion injection followed by waterflooding in the Midway-Sunset Field (McAuliffe, 1973).

Several waterflood recovery process patents assigned to Texaco, Inc., describe laboratory core studies in which blocking emulsions were produced <u>in situ</u> by injection of surfactant mixtures (Varnon, et al., 1979, Schievelbein, 1979, and Schievelbein, et al., 1979). The conditions under which these experiments were performed (relatively high salinity, presence of divalent ions, crushed limestone cores) allow us to infer the creation of water-in-oil emulsions. Cooke, in laboratory experiments, has observed that a viscous oil-external emulsion may be responsible for the large increase in pressure gradient that is observed immediately behind the displacement front during alkaline waterflooding under saline conditions (1974). A recent waterflood patent assigned to Mobil Oil Corporation relates to the creation of a plugging emulsion within a high salinity stratified reservoir (Hurd, 1984). The surfactant/water/oil emulsion described in this patent is likely oil external.

Special Requirements

Special requirements must be met in order to extend the use of emulsions as mobility buffers to steamflood conditions. The chemicals used and the emulsions produced must be stable for long periods of time at steamflood temperatures. Some chemical surfactants such as sulfates would be expected to hydrolyze too rapidly under such conditions.

Since many steamfloods are performed in the laboratory and in the field with steam generated from fresh water, the level of salinity in the steamflooded channel is expected to be low. Consequently, the emulsion must be stable under low salinity conditions.

Conditions within the steamflooded channel are likely to be more favorable to the presence of oil-in-water emulsion than water-in-oil emulsion. Fresh water systems are generally associated with highly stable oil-in-water emulsions (Mayer, et al., 1982). Entrapment of oil droplets, a mechanism for reducing permeability to water, is associated with alkaline floods performed using fresh water.

Emulsion Formation

Oil-in-water emulsions can be produced by mixing oil with an aqueous solution of emulsifier (agent-in-water method) or by utilizing the naturally occurring surfactants already present in some oils (agent-in-oil method). Either method is suitable for creation of the emulsion above ground and then injection of that emulsion into the reservoir.

In situ formation of oil-in-water emulsions adds the requirement that the emulsification proceed spontaneously or at least with very little energy input due to mixing. Most such systems are associated with the agent-in-oil procedure and spontaneous emulsification to oil-in-water emulsions does often occur when mixing aqueous caustic and petroleum oils containing naphthenic acids. Some researchers propose that diffusion of the naturally occurring surfactants across the interface is the mechanism that causes this phenomena (Becher, 1983).

Emulsification with caustic is possible with oils that have a total acid number (TAN) greater than 1.5 mg KOH/gm oil. Below 1.5, the oils will either not emulsify or will form water-in-oil emulsions. The rate of emulsification with caustic is much faster than emulsification with surfactant mixtures, which is a characteristic property for emulsions generated via the agent-in-oil procedure (Becher, 1983).

Although much literature exists regarding the spontaneous formation of thermodynamically stable microemulsions, which do not contain droplets large enough to cause permeability reductions, little information is available regarding the spontaneous formation of macroemulsions which contain larger oil droplets and are not thermodynamically stable. However, review of the literature does indicate that some aqueous surfactant mixtures (agent-in-water) may promote the spontaneous formation of macroemulsions. Researchers at the University of Texas have concluded that spontaneous emulsification - distinctly different from the low tension processes - between oil and an aqueous phase containing petroleum sulfonates occurs with specific hydrocarbons and not with others (Cash, et al., 1975 and Schecter and Wade, 1976). The spontaneous emulsification observed occurred only in a narrow region at the interface and was not observed to occur for paraffins or for crude oil.

Emulsion Properties

In most cases, the type of an emulsion (oil-in-water or water-in-oil) can be predicted by the appearance of the emulsion. In general, oil-in-water emulsions will appear to be chocolate or brown in color and dilute easily with water, although creaming will occur eventually if agitation ceases. An important property of the emulsion is the droplet size distribution. If the droplets are too small, they may tend to slowly solubilize into the continuous phase or not block at all, and if they are too large, creaming and coalescence may become problems. The oil droplets in macroemulsions normally are between 1 and 50 microns in diameter and are easily visible with an optical microscope. Emulsions produced via the agent-in-oil procedure usually have more uniform droplet sizes and are quite stable (Wasan, 1976). The viscosity of oil-in-water emulsions remains low enough to pump easily. The electrical conductivity of oil-in-water emulsions tends to be that of the aqueous phase.

Water-in-oil emulsions, on the other hand, generally appear to be black in color, do not dilute with water, and have electrical conductivity lower than that of the brine. The viscosities may be very high and thixotropic.

Blockage Mechanisms

McAuliffe's concept of the mechanism by which an oil-in-water emulsion can cause a permeability reduction is shown in figure 1. In this case, the oil droplet is large enough to cause blockage by lodging within the pore throat. For this situation, the flow of a dilute, stable emulsion in a porous media is similar to a filtration process. If the pressure gradient across the drop becomes great enough, the drop may be forced on through the pore throat. Another process for reducing permeability has been observed by Soo. When emulsions are injected into a porous media micro-model, drops not only block pores of throat sizes smaller than their own, but they are also observed to capture on pore walls and in crevices (Soo, et al., 1984).

It is important to observe that a reduction in permeability from emulsion plugging may not necessitate that the median droplet size equal or exceed the median pore throat diameter. Competition from an ensemble of smaller droplets "crowding" a single pore throat would have the same effect in blocking a pore throat as would one large droplet as shown in figure 1. Another important (but speculative) mechanism of emulsion plugging to consider, is the decrease in relative permeability of the gas (steam) phase due to the presence of an additional competing emulsion phase. Here again, emulsion droplets smaller than the median pore throat size in the porous structure would possibly play a role in the overall blocking mechanism.

Finally, permeability reductions attributed in the literature to the formation of water-in-oil emulsions are evidently due to the high viscosity of those emulsions or to the formation of an oil film (lamella) across the pore throat (Cooke, 1974).

EXPERIMENTAL

Study of Emulsification

The crude oils selected for the study are a 19° API California crude from the Wilmington Field and a 33° API mid-continent crude from the Delaware-Childers Field in Oklahoma.

Emulsions were tested by mixing an emulsifier (either caustic or commercial surfactants dissolved in water) and the crude oil, then heating the sealed container to 110° C in an oven. After heating, the sample was removed from the oven and placed in a mechanical shaker for 15-20 minutes, then returned to the oven. This procedure was repeated three times before the sample was left in the oven for observation.

Emulsification of the Wilmington oil with caustic proceeds almost spontaneously. The stability of 50 percent oil-in-water emulsions produced with Wilmington oil and caustic is given in table 1. These oil-in-water emulsions are quite stable at 110° C for long periods of time. The optimal concentration of sodium hydroxide occurs at 0.42 percent NaOH where a uniform single-layer oil-in-water emulsion is produced. At higher NaOH concentrations, the increasing ionic strength of the solution results in formation of upper layer water-in-oil emulsions.

Droplet size distributions for oil-in-water emulsions were determined with a Model TA II Coulter Counter. The quantitative results obtained with the Coulter Counter were verified by qualitative observations with an optical microscope. The droplet size distribution for the Wilmington oil at optimal NaOH concentration is given in figure 2 along with the size distributions for some other oil systems. The pore size distribution for a 300 md Berea core is also given for comparison.

The total acid numbers (TAN) and the experimentally determined optimal NaOH concentrations for Wilmington and other viscous, asphaltic crude oils are given in table 2.

Oils with low TAN such as the Delaware-Childers crude cannot be emulsified with caustic. Attempts were made to produce an oil-in-water emulsion which is stable at 110° C by using petroleum sulfonates of different average weights as the emulsifying agent. The Delaware-Childers oil was mixed with the aqueous emulsifier at a ratio of 1:6 and tested according to the procedure previously described. If all of the oil emulsified, this would correspond to a 14.3 percent oil-in-water emulsion. Results of emulsification tests performed with petroleum sulfonates at 3.75 percent active concentration and Delaware-Childers oil are given in table 3. Also given are results for mixtures of 3.75 percent petroleum sulfonates with 2.5 percent SE-463, a water soluble ethoxylated sulfonate furnished by GAF Chemical Company. The volumes of the layers were observed after 16 hours at 110° C. The largest volume of stable oil-in-water emulsion was obtained for the mixture of 3.75 percent Petrostep 420, a medium equivalent weight petroleum sulfonate, and 2.5 percent SE-463 at 4.25 percent NaCl.

All of these systems, after shaking, separated into two distinct layers. At low salinities, the lower layer consists of oil-in-water emulsion which is stable for some period of time, depending on the particular system. At higher salinities inversion occurs, and the lower layer separates as a clear liquid with no oil droplets - the upper layer then becoming a water-in-oil-emulsion.

The optimal system consisting of 3.75 percent Petrostep 420 and 2.5 percent SE-463 was particularly stable and emulsions up to 33 percent Delaware-Childers oil were easily prepared. The size distribution for this emulsion is given in figure 2 and is broader than the size distribution for other emulsions - typical for an emulsion prepared via the agent-in-water procedure.

Since the systems with Delaware-Childers oil did not result in spontaneous emulsification - desirable for performing emulsification *in situ* - to macroemulsions, a procedure similar to an "emulsifiable concentrate" was tested. The system tested resembles dispersant mixtures used for treatment of oil spills (Blanchard and Dudley, 1976). These mixtures consist of surfactants dissolved in an oil compatible solvent. The dispersant formulated consisted of sorbitan partial fatty ester, dodecylbenzene sulfonate, and isobutyl alcohol in methylisobutyl ketone. Upon contact with the Delaware-Childers oil and water, a macroemulsion forms spontaneously. Although the quantitative size distribution has not yet been determined, observation with the optical microscope revealed droplets in the 5-10 micron range.

Coreflood Test Procedure

Laboratory coreflood experiments were performed to test the effectiveness of emulsion blocking in improving sweep efficiency at elevated temperatures. The emulsions, prepared as previously detailed, were diluted to 0.5 volume percent oil before injection into the cores. The emulsion reservoir was stirred slowly to prevent the dispersed oil droplets from creaming. Creaming was more a problem with the light oil emulsion than with the heavy oil emulsion.

Berea cores (10 in. x 1.5 in.) used in the experiments were fired at 800° F to minimize the effects of clay-water reactions. After firing, the cores were saturated with brine, mounted in a Hassler type core holder, and placed in a temperature controlled box. After determining initial absolute permeability, the cores were either left oil-free or saturated with oil and waterflooded to residual oil saturation.

Fluid injection, pressure monitoring, and temperature were controlled by an HP85 microcomputer system. Injections were done at constant flow rate with a Constametric III metering pump, from which the filters were removed.

Coreflood Tests with Oil-Free Cores

The coreflood experiments were at first performed at ambient temperature and then extended to hot water conditions at 110° C as an approach to saturated steam conditions. Pilot experiments with the light mid-continent crude were extended to the heavier California crude oil, with an actual steamflood at saturated steam conditions (160° C) to test the steam stability of an "emulsion block" created with the heavier oil. The data for these coreflood tests are summarized in table 4.

Figures 3 and 4 illustrate the effects on effective permeability to water of injecting the 0.5 percent oil-in-water emulsions created from Delaware-Childers oil. At 25° C, a 68 percent reduction in permeability occurred after injecting 9.5 PV of emulsion. At 90° C, 10 PV of emulsion resulted in a 95.2 percent reduction in permeability, with most of the reduction occurring within 3 pore volumes.

Figures 5, 6, and 7 are the permeability reductions that resulted when injecting 0.5 percent emulsions produced from the Wilmington oil and caustic. The temperatures are, respectively, 25, 90, and 110° C. The reductions in permeability were from 84 to 88 percent, with the major part of the reduction occurring within one pore volume of emulsion injection.

These experiments were conducted at constant flow rate. Blocking effects at constant pressure (more similar to field conditions) would probably show more dramatic effect. In all of the experiments with injected emulsions, the effective permeability to water was decreased far more than an equivalent amount of residual oil would have reduced the permeability. The emulsion droplets are more efficient at reducing the effective permeability of a core than is the same amount of oil that is not emulsified.

Similar results were obtained when injecting an externally produced emulsion into a core which would be steamflooded. The results (table 4) show that the emulsion block (created with Wilmington oil) was stable at steamflood conditions. This experiment was conducted with a 25 in. core and saturated steam at 160° C. Before emulsion injection, permeabilities were measured before and after steam to make sure the steamflood itself did not cause a permeability reduction. A 77 percent reduction in permeability from external emulsion injection was observed under these steamflood conditions providing strong evidence for the development and utilization of this type of blocking procedure in the field.

Emulsion Injection into Cores Containing Residual Oil

These experiments were performed because of uncertainty about the effect of residual oil on an "emulsion block". In the case of residual oil remaining in the core, the effective permeability to water is much lower at the beginning of emulsion injection than with an oil-free core. The results are summarized in table 5.

In one experiment, emulsion injection was begun after waterflood and in the others emulsion injection was begun after tertiary recovery. The number of pore volumes of emulsion injected was 10, 7, and 8, respectively. The reductions in effective permeability, 52, 33, and 56 percent, were significant, but not as high as when using oil-free cores.

These experiments also illustrate a problem in performing corefloods in a one-dimensional coreflood apparatus - the situation of gravity override is difficult to simulate. The two-dimensional steamflood model now being installed at NIPER will allow a more realistic simulation of field steamfloods and the resultant channeling due to gravity override.

In Situ Emulsification

Coreflood experiments designed to cause permeability reductions by *in situ* creation of oil-in-water emulsions have been less successful than externally produced emulsions, but still show significant reductions in permeability. The data are summarized in table 6.

The first two tests were performed in the usual manner of saturating the core with Wilmington oil and then waterflooding to residual oil saturation, resulting in oil saturation of 45 and 49 percent, respectively, before caustic injection. After injection of caustic slugs, the effective permeabilities were reduced 27 and 25 percent, respectively.

In the third test, the core was not saturated with oil before waterflooding and the residual oil saturation was 34 percent before injection of caustic. Under this condition, the reduction in effective permeability increased to 43 percent. In all three tests, oil-in-water emulsions were produced from the core which had droplet size distributions appropriate to cause pore throat blockages. These three tests again illustrate that it is difficult to simulate in a one-dimensional model the conditions which exist in an actual reservoir after a steamflood, but that it is possible to create "emulsion blocks" *in situ* under appropriate conditions.

Another experiment was performed using Delaware-Childers oil and the dispersant mixture described previously. Sand (70 mesh) was packed into a 1.25 in. x 5 in. glass tube. The sandpack was placed in a vertical position and gravity flow (constant WP) was utilized to saturate with oil and waterflood to residual oil. The flow rate to water after waterflood was measured at 7.1 ml/minute.

After dispersant introduction, the flow rate was reduced to zero and would not resume until increased pressure caused the emulsion formed to be forced on through the sandpack. This experiment draws more attention to the probability that emulsion blocks will be more stable at constant pressure than at constant flow.

Conclusions

After creating foam with known foaming agents and contacting that foam with crude oils, the authors have observed emulsified droplets of oil within the liquid interfaces between the gas bubbles of the foam; however, we have not contributed (yet) to the question of whether "foam" blocking is really emulsion blocking.

We have shown that emulsions can be formed that are stable at higher temperatures, and survive on dilution with fresh water. They have the theoretically assumed drop sizes to block pores in a porous medium at elevated temperatures and in the presence of saturated steam. Emulsion blocking occurs also in the presence of residual oil. *In situ* formation of emulsions by injecting the emulsifying agent was shown to cause blocking, but further research in needed to increase its effectiveness and to prepare the technique for commercialization.

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[2]National Institute for Petroleum and Energy Research (NIPER, a division of IIT Research Institute).

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TABLE 1. Emulsification of Wilmington Crude Oil with Caustic

NaOH(%)	Vol (ml.)		Apparent emulsion type		Phase Volume (ml.)					
	Oil	Aqueous			Room temperature		4 hrs. at 110° C		8 days at 110° C	
			Upper	Lower	Upper	Lower	Upper	Lower	Upper	Lower
0.00	3.0	3.0	w/o	w	5.0	1.0	3.3	2.7	3.1	2.9
0.03	3.0	3.0	o/w	o/w	5.5	0.5	5.3	0.7	3.6	2.4
0.08	3.0	3.0	o/w	o/w	4.5	1.5	4.1	1.9	3.5	2.5
0.17	3.0	3.0	o/w	o/w	5.1	0.9	4.7	1.3	3.8	2.2
0.25	3.0	3.0	o/w	o/w	4.8	1.2	4.4	1.6	0.4	5.6
0.42	3.0	3.0	o/w	o/w	5.7	0.3	6.0	0.0	0.1	5.9
0.58	3.0	3.0	w/o	o/w	2.7	3.3	2.8	3.2	2.8	3.2
0.75	3.0	3.0	w/o	o/w	3.5	2.5	3.2	2.8	1.7	4.3
1.00	3.0	3.0	w/o	o/w	3.5	2.5	3.2	2.8	3.0	3.0

TABLE 2. - Emulsification of Asphaltic Crude Oils with Caustic

Oil	Viscosity (cps)	Wt. Percent S	Wt. Percent N	Acid Number	Optimal NaOH Concentration (%)
Wilmington 5G	175			2.04	.42
Wilmington B66099	370	1.73	.72	2.31	.18
Midway-Sunset B76067	650	1.05	.73	4.15	.42
Hasley Canyon B77023	>1100	5.5	.96	.68	None

TABLE 3. - Static Emulsification Tests Performed with Surfactants and Delaware-Childers Oil

Petroleum Sulfonate	Average eq. wt.	Ethoxylated sulfonate	NaCl (%)	Volume, oil-in-water emulsion 110° C (16 hours elapsed) (ml)
Witco-40 (3.75%)	335	None	0	5.9
			2.12	6.0
			4.25	5.9
Witco-40 (3.75%)	335	SE-463 (2.5%)	0	6.0
			2.12	6.0
			4.25	6.0
PetroStep-420 (3.75%)	420	None	0	5.9
			2.12	6.2
			4.25	0
Petrostep-420 (3.75%)	420	SE-463 (2.5%)	0	6.0
			2.12	6.1
			4.25	6.9 (optimum)
Witco-18 (3.75%)	495	None	0	0
			2.12	0
			4.25	0
Witco-18 (3.75%)	495	SE-463 (2.5%)	0	6.5
			2.12	0
			4.25	0

TABLE 4. - Injection of Externally Produced Emulsion into Oil-Free Cores

Temp. (°C)	Emulsion Injected (PV)	Permeability Absolute (md)	Permeability Final (md)	Permeability Reduction (%)	Flow rate (cc/min)
		Delaware-Childers Oil (Light)			
25	9.5	219	71	68.0	3.4
90	10.0	148	7	95.2	3.4
		Wilmington Oil (Heavy)			
25	8.9	266	31	88.3	3.4
90	9.9	74	12	84.3	3.4
110	8.5	187	26	86.1	3.4
160	6.5	90	21	76.7	5.0

TABLE 5. - Injection of Externally Produced Emulsions into Cores Containing Residual Oil
Delaware-Childers Oil - 25° C

Emulsion Injected (PV)	Permeability Absolute (md)	Before emulsion (md)	Final (md)	Reduction (%)	Flow rate (cc/min)
10.0	285	33	16	52	3.4
7.0	324	26	18	33	3.4
8.0	297	84	38	56	3.3

TABLE 6. - *In Situ* Emulsion Formation
Wilmington Oil - 50° C

Emulsion Injected (PV)	Permeability Absolute (md)	Before emulsion (md)	Final (md)	Reduction (%)	Emulsifier	Flow rate (cc/min)
0.45	325	45	33	27	0.55% NaOH	3.4
0.47	257	24	18	25	1.06% NaOH	3.4
0.83	1,400	88	50	43	1.06% NaOH	3.4

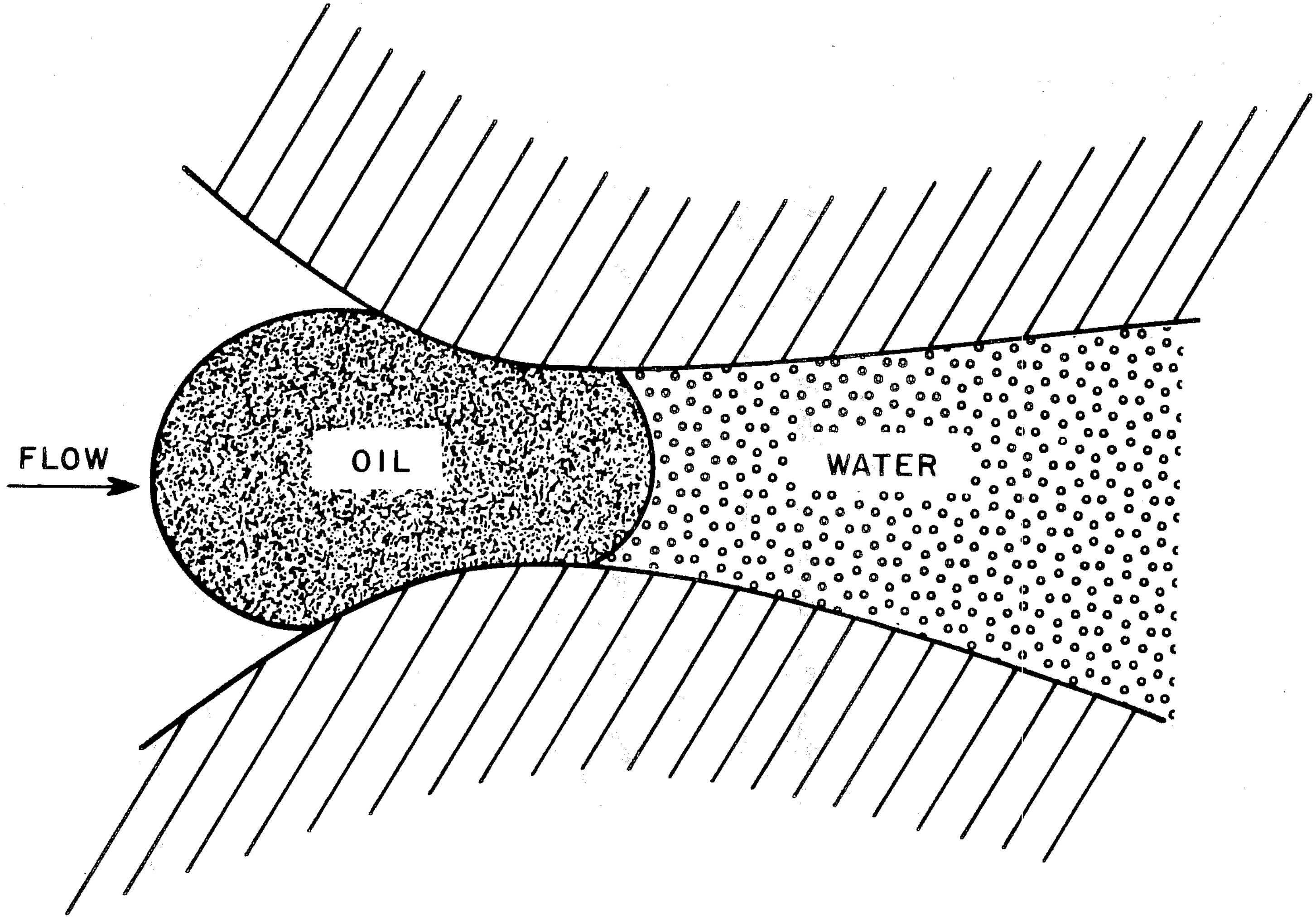

FIGURE A-1. Pore throat with oil droplet blocking water flow.

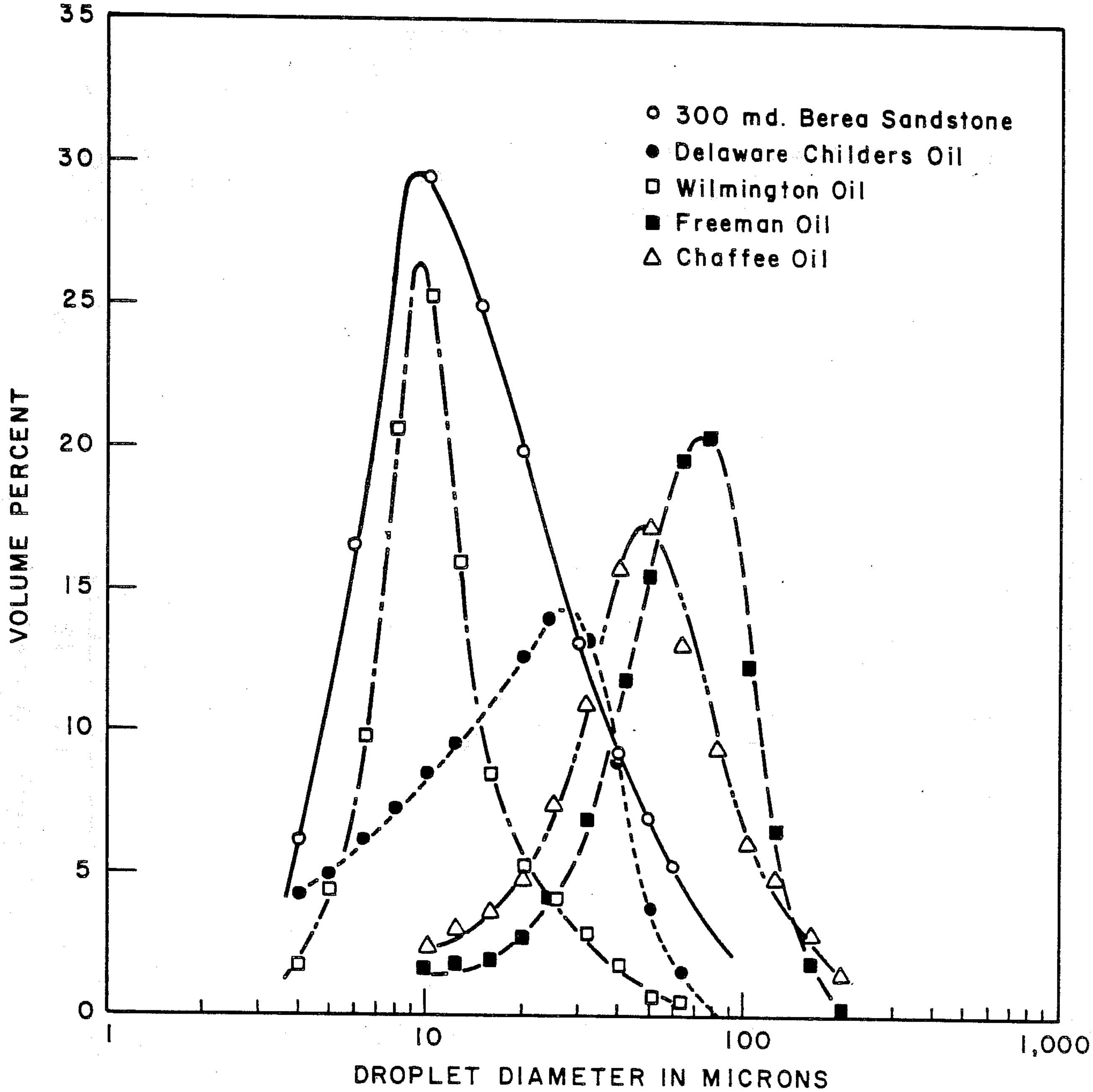

FIGURE A-2. Droplet size distribution for emulsions.

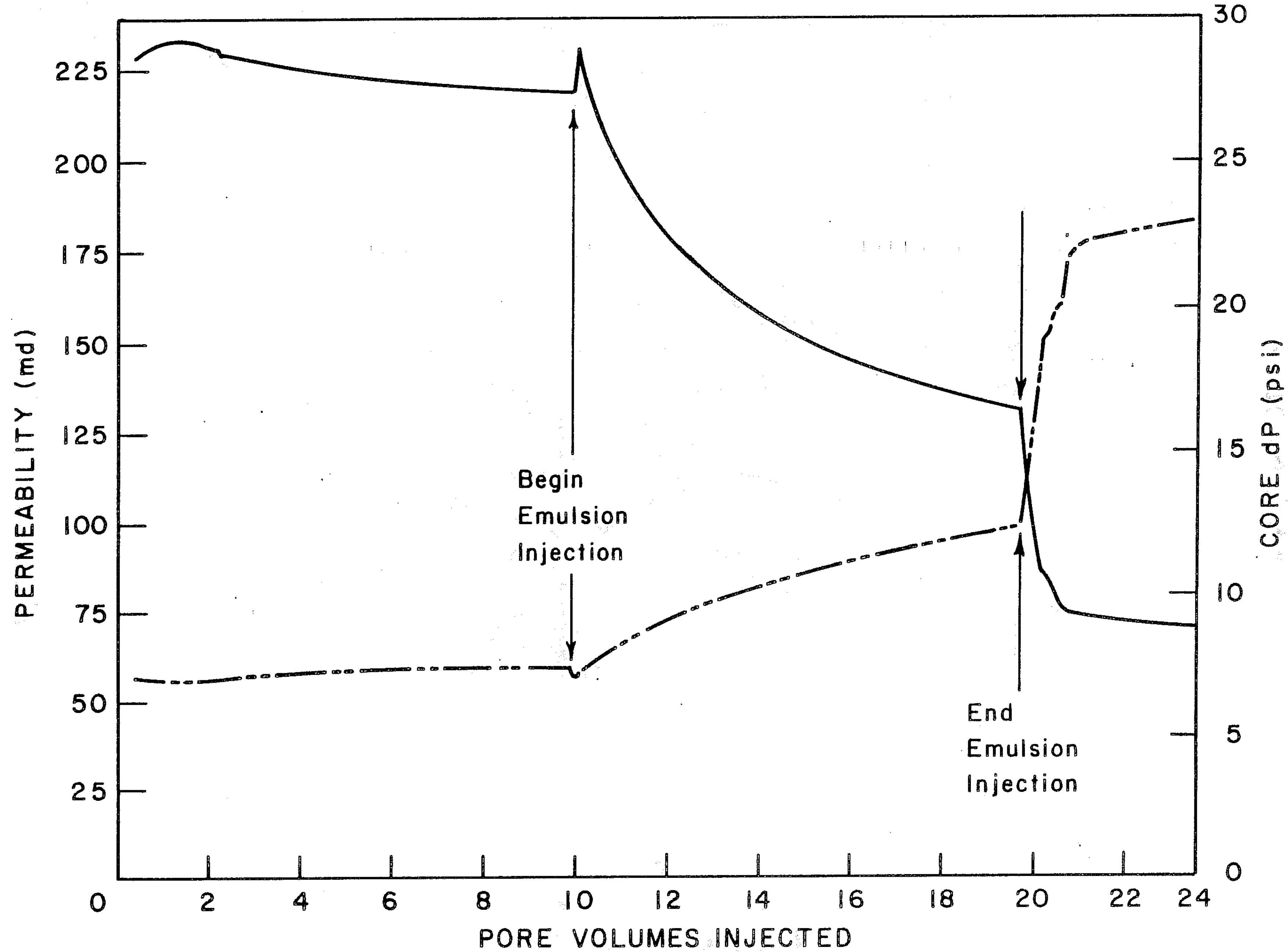

FIGURE A-3. Permeability reduction - 25° C Delaware-Childers oil.

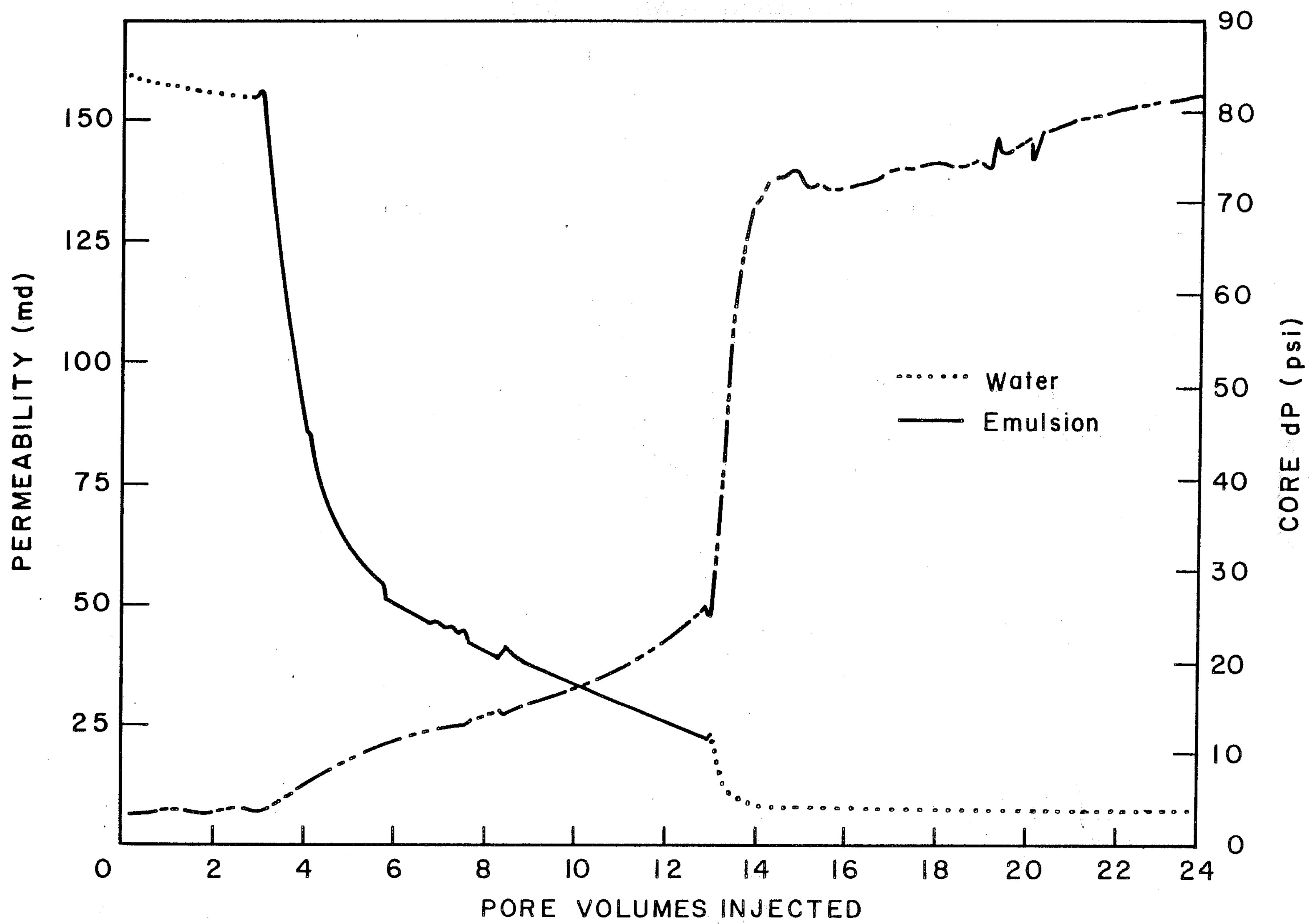

FIGURE A-4. Permeability reduction - 90^{o} C Delaware-Childers oil.

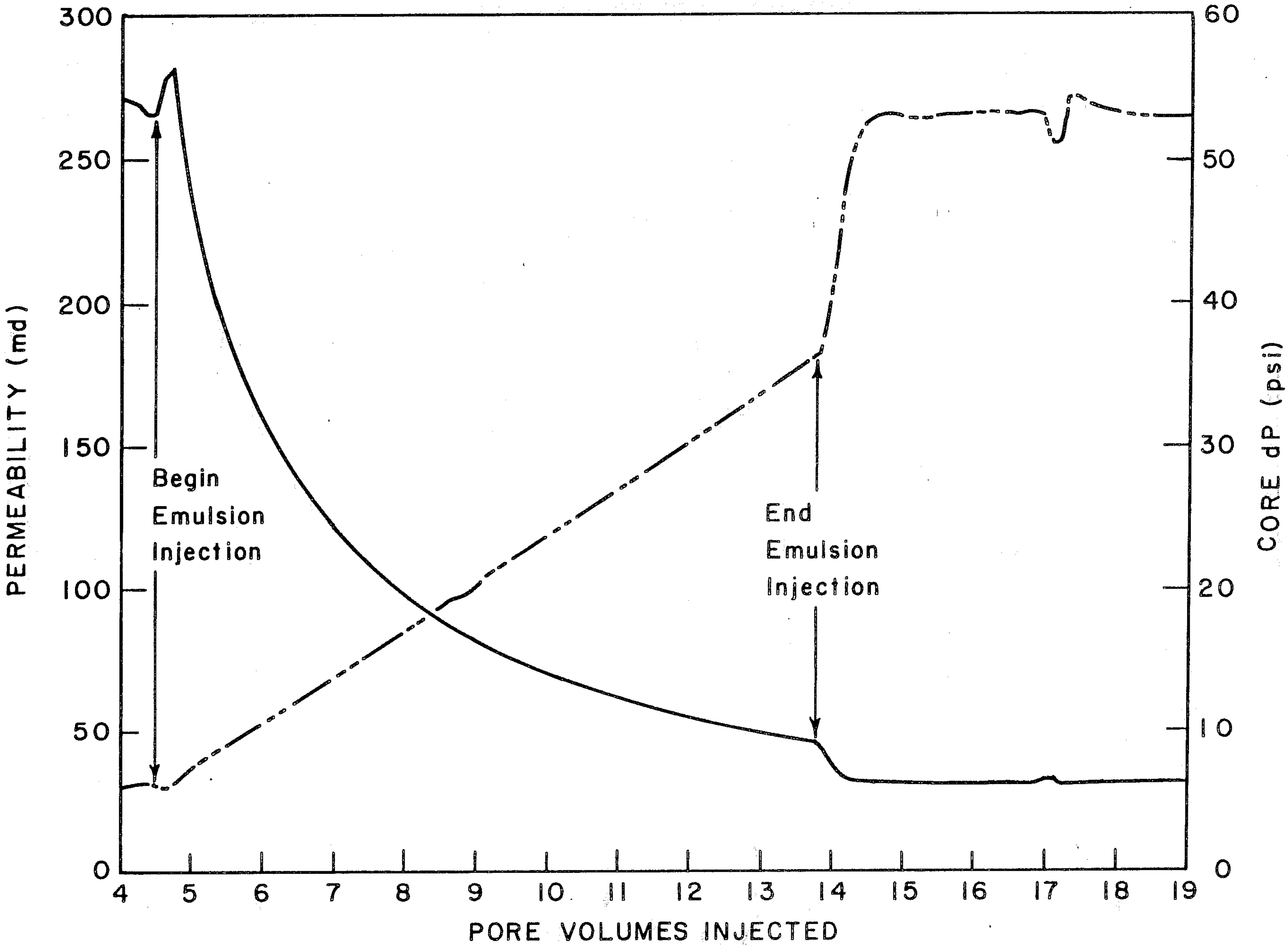

FIGURE A-5. Permeability reduction - 25^{0} C Wilmington oil.

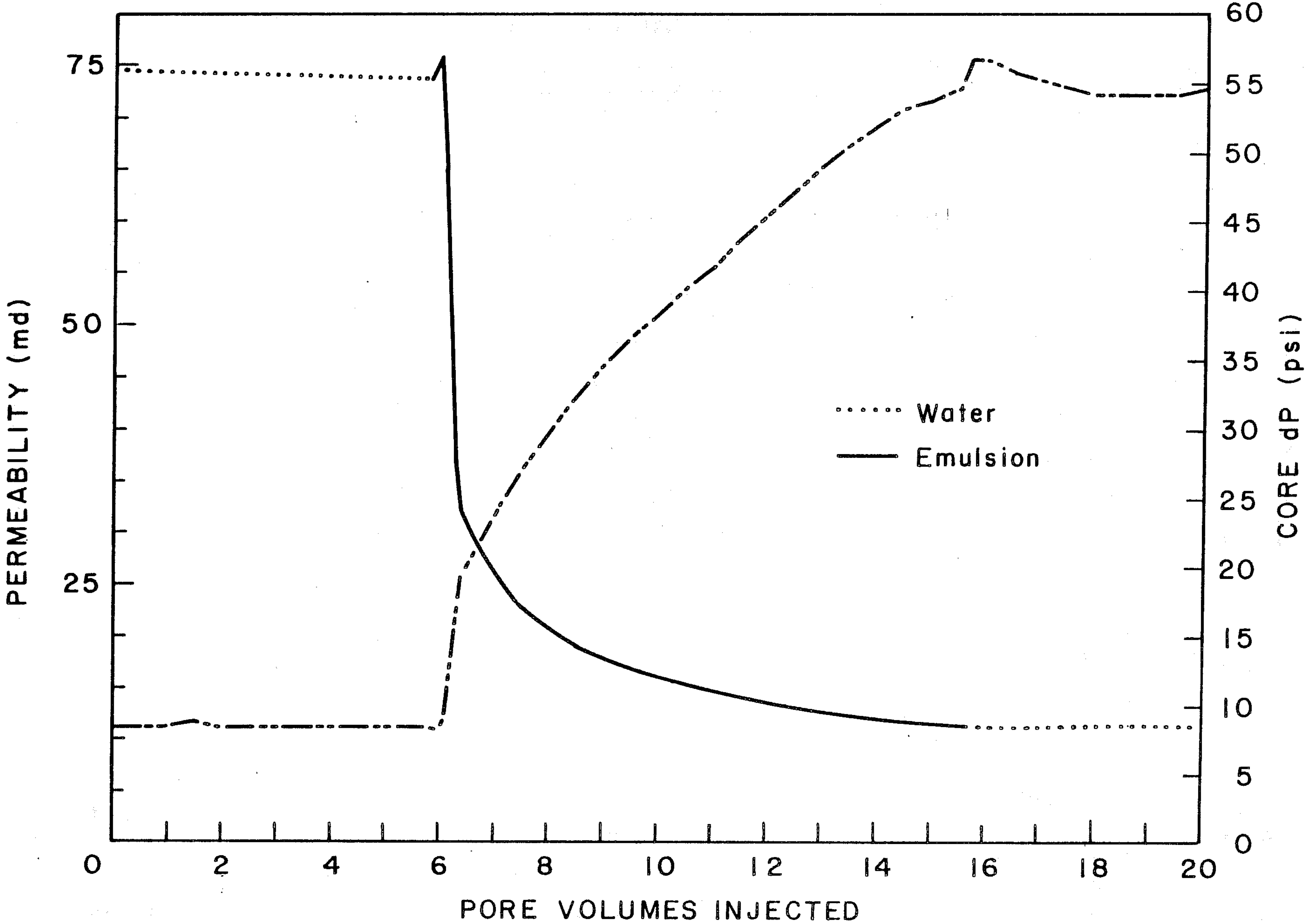

FIGURE A-6. Permeability reduction - 90^{0} C Wilmington oil.

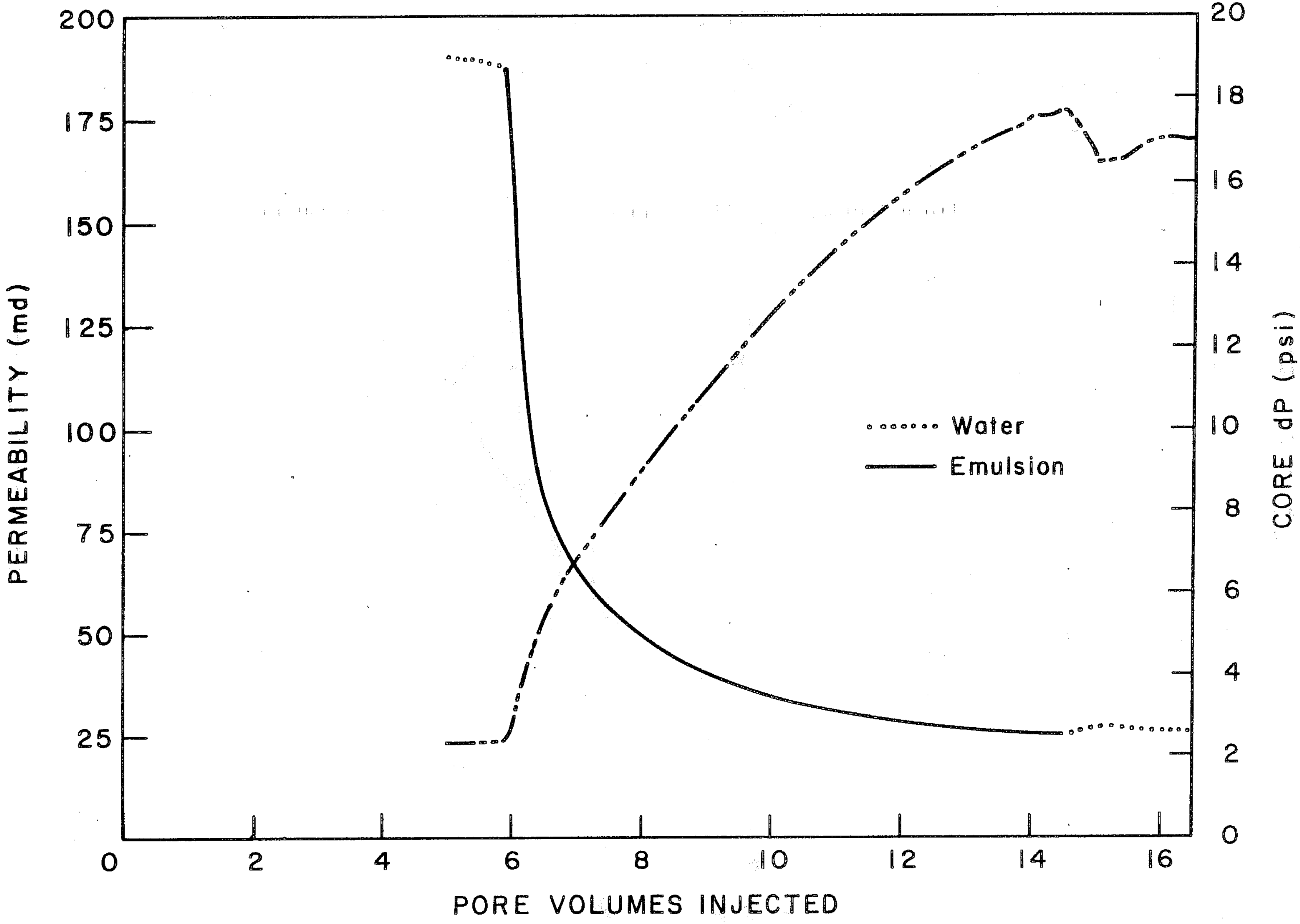

FIGURE A-7. Permeability reduction - 110^{0} C Wilmington oil.